Pall Corporation

Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance

(Pre-Combustion Capture)

2011 NETL CO_2 Capture Technology Meeting
Pittsburgh, PA

Scott D. Hopkins
Pall, Technical Director
August 22-26, 2011

Agenda

1. Introduction to Pall Corporation (www.pall.com)
2. Project Overview
3. Technology Fundamentals
4. Progress and Current Status
5. Plans for Development and Commercialization

PALL Pall Corporation

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- **Annual sales of +US $ 2.5 Billion**
- **78 Locations in 34 Countries**
- **Approximately 10, 000 Employees**
- **Traded on the NYSE (PLL)**

Offices and Plants

Argentina
Australia
Austria
Belgium
Brazil
Canada
China
France
Germany
Hong Kong
India
Indonesia
Ireland
Italy
Japan
Korea
Malaysia
Mexico
Netherlands
New Zealand
Norway
Poland
Puerto Rico
Russia
Singapore
South Africa
Spain
Sweden
Switzerland
Taiwan
Thailand
United Arab Emirates
United Kingdom
United States
Venezuela

<u>Market Segments</u>

Pall Life Sciences
- Medical
- Biopharm

Pall Industrial
- Aerospace & Transportation
- Food & Beverage
- Fuels & Chemicals
- Industrial Manufacturing
- Materials
- Microelectronics
- Power Generation
- Water

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Project Overview

Funding:

- $1,517,000 total
- $1,207,000 (NETL)
- $310,000 (Pall)

Performance:

- Oct 1, 2009 to Sept 31, 2012

Participants:

- Pall Corporation
- Cornell University
- Georgia Institute of Technology
- Oak Ridge National Laboratory
- Southern Company

Objectives:

- Develop an economic, high temperature and pressure, hydrogen separation membrane system for CO_2 capture that resists moderate levels of contaminants, typical in gasified coal.
- Create an advanced palladium alloy for optimum hydrogen separation performance using combinatorial material methods for high-throughput screening, testing, and characterization.
- Demonstrate durability by long term testing of a pilot membrane module at a commercial coal gasification facility.
- Understand long term effects of the coal gasifier environment on the metallurgy of the membrane components.

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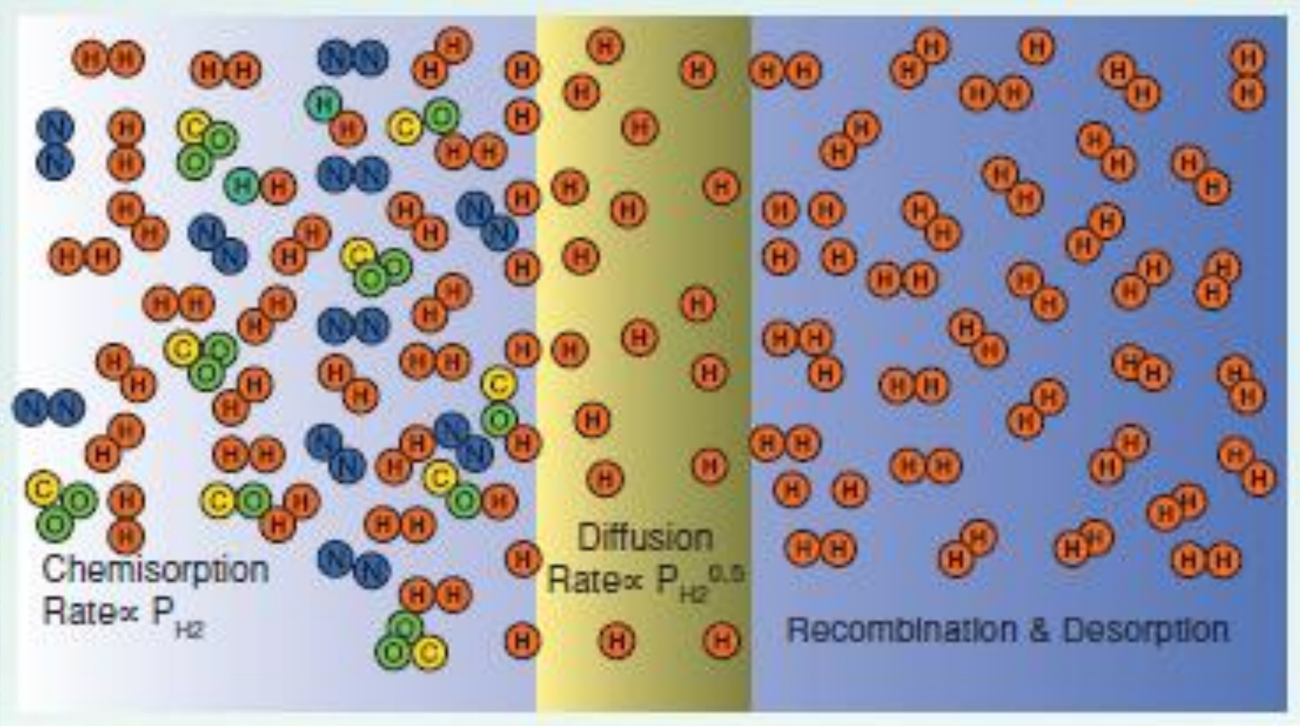
Why Pd Membranes



Offer very high selectivity for hydrogen over other gases present in feed stream

Transport is based on pressure – driving hydrogen atom diffusion through the interstitials of metal lattice

Pd alloys are durable

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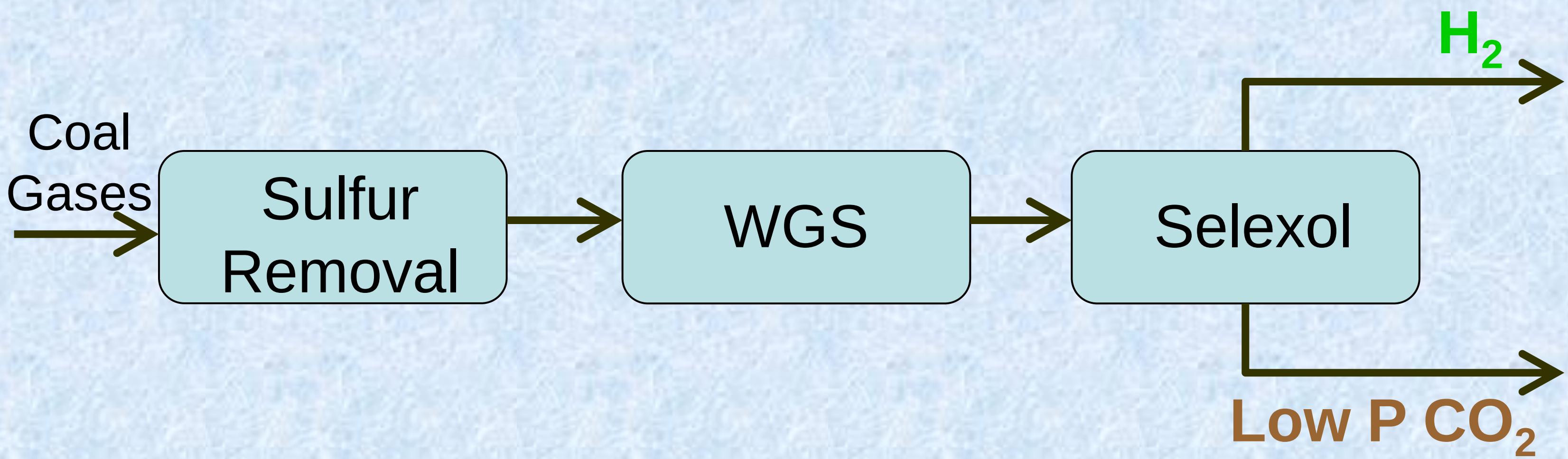
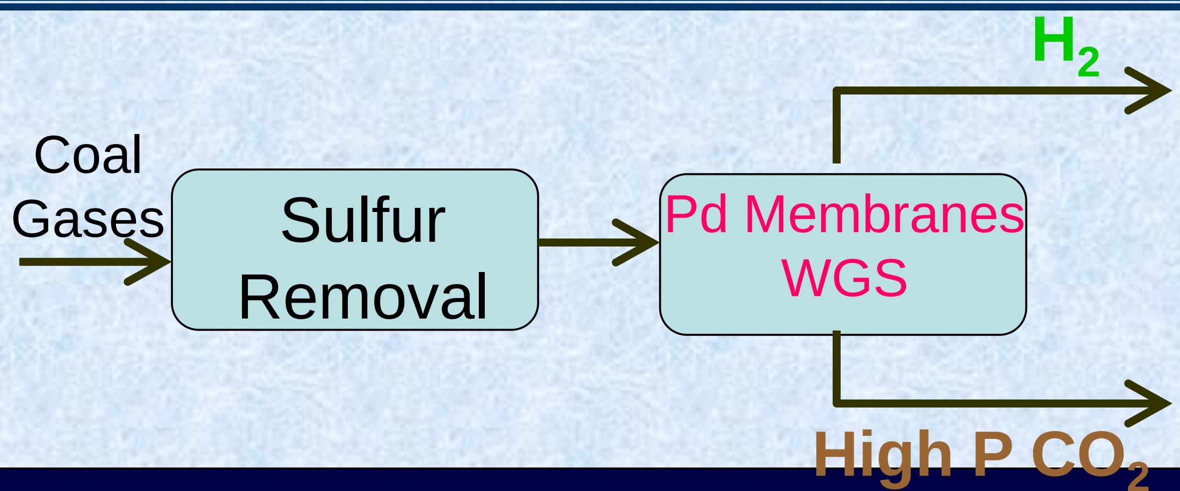
The Technology – In Operation

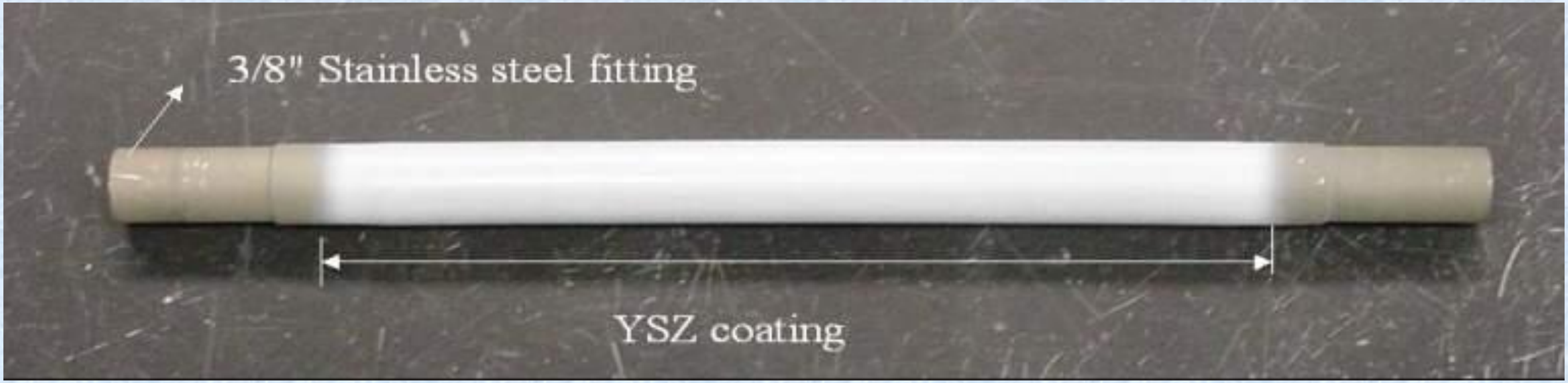
CO_2 Capture by the Conventional Technology

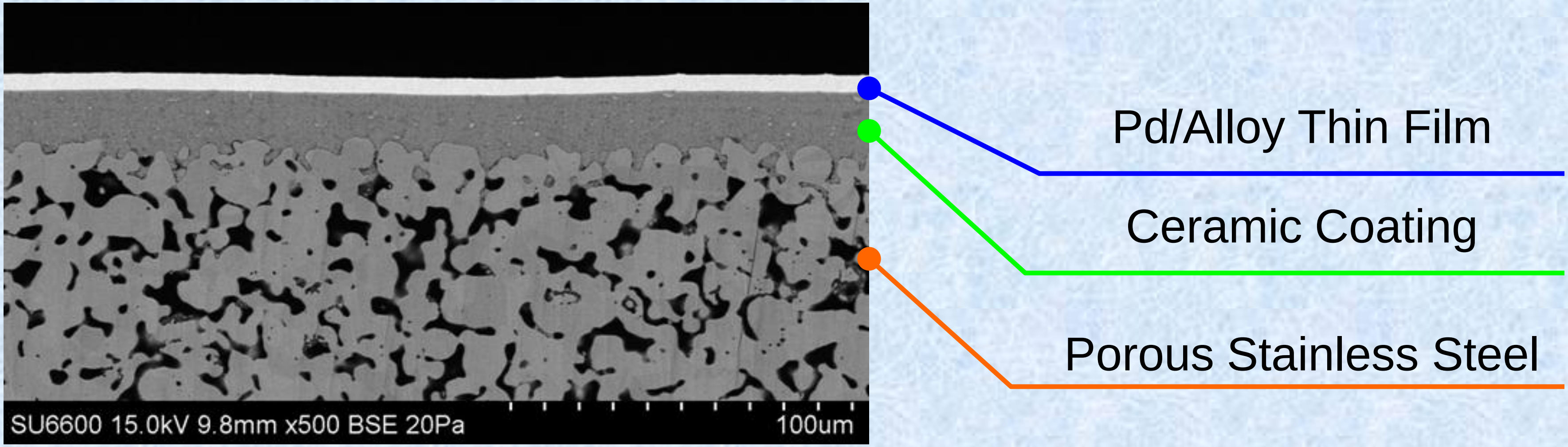


CO_2 Capture by Pd Membrane Reactor



The Technology – Membrane Support





The Technology – Membrane Element

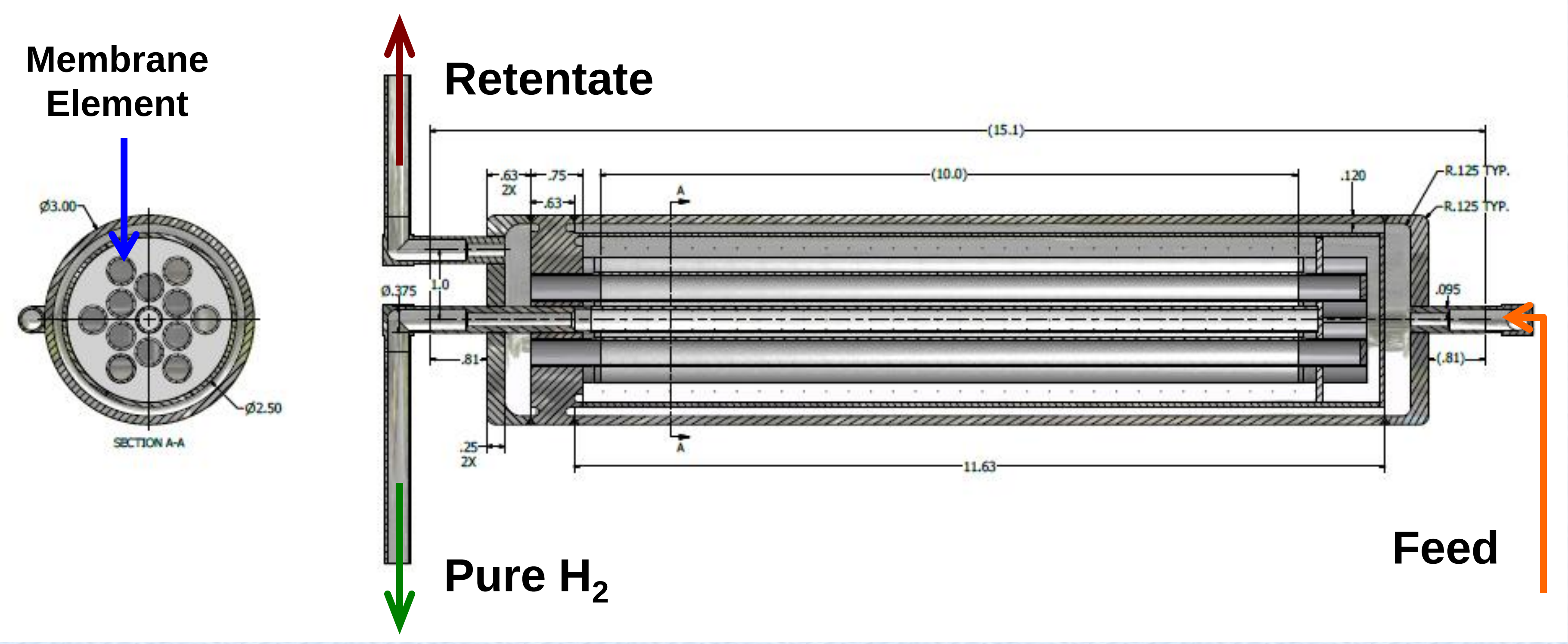
Pall's palladium alloy membrane system will include:

- Pd alloy thin film
- Porous 310 stainless steel support tube; solid end fittings
- Nanoporous yttria-stabilized zirconia (YSZ) substrate
- Directly welded to tube sheet without need for sealing
- Uniform thermal expansion of housing and module.

The Technology – Membrane Module

A Small Size Module

- Twelve 12-inch membrane tubes
- Membrane area 140 inch^2 (900 cm^2)
- Pure H_2 flux 70 SLPM under typical conditions



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The Technology - Advantages & Challenges

- Any alloy composition can be fabricated
- Membrane elements can be assembled by conventional welding
- CO_2 is produced at a higher pressure
- The hydrogen product is high purity product H_2
- Hydrogen is produced at higher temperature
- Lower parasitic loading, for instance CO_2 compressing

- Lack of ternary phase diagrams for selecting potential S/C resistant alloys
- Membranes must remain defect-free for years
- Long-term microstructural changes are unknown
- Long term H_2 flux and separation data are unknown

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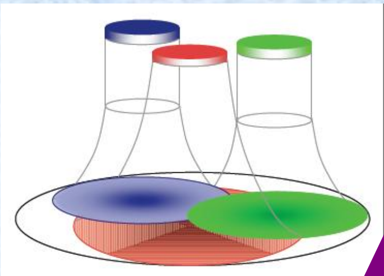
Project Milestones and Timeline

Note 6 month no cost extension

Note (2) missing quarters due to contract negotiations

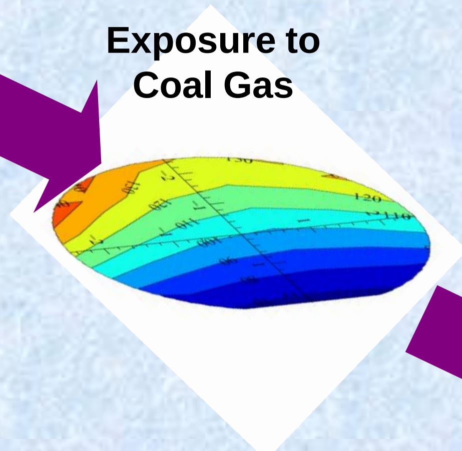
		2009		2010				2011		2012				2013	
		Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2
1	Project management and planning														
2	Literature and patent search Milestone 1–Report demonstrating understanding														
3	Design and modeling of binary and ternary Pd alloys Milestone 2 – Report on use of combinatorial method														
4	Construct & test 15 cm^2 active area prototypes Milestone 3 – Report on testing small membranes														
5	Scale up active surface area from 15 cm^2 to 75 cm^2 Milestone 4 – Report on testing scaled up membranes														
6	Construct and test a working membrane module Milestone 6 - Report on long term performance														
7	Provide complete analysis of relevant data sufficient to Permit economic evaluation of the process														
	Milestone 7 – Report on advancement necessary to commercialize														

Combinatorial Alloy Development Workflow

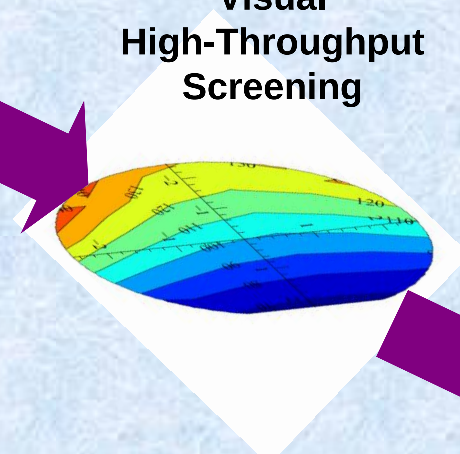


Compositional Spreads

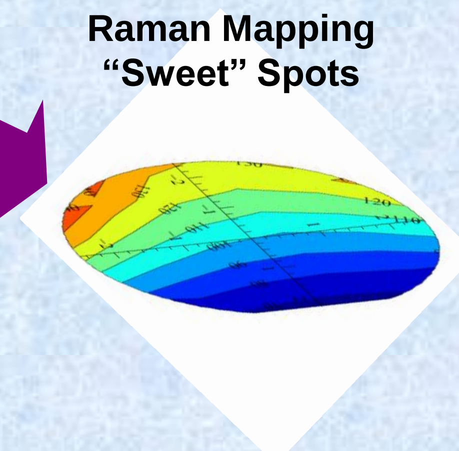
Exposure to Coal Gas



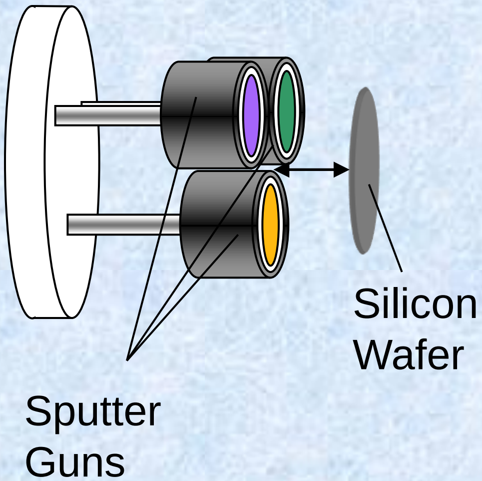
Visual High-Throughput Screening

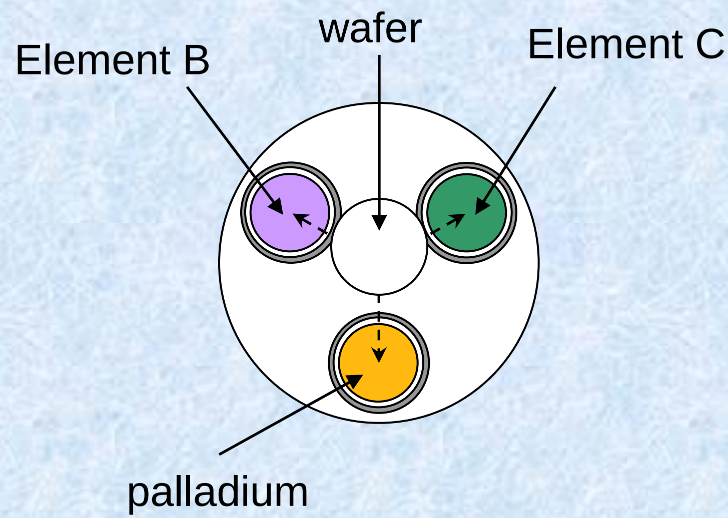


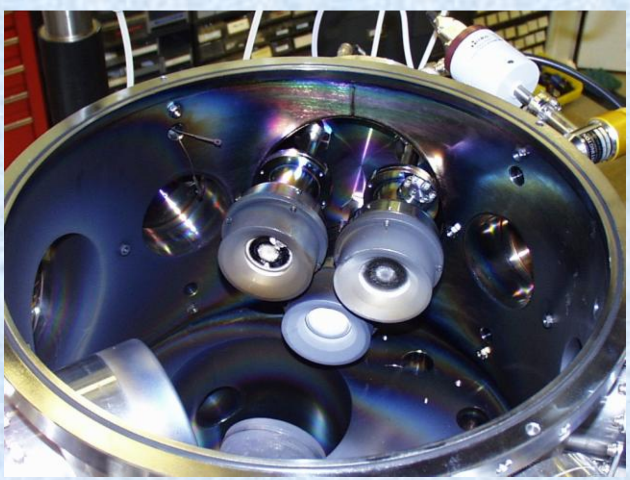
Raman Mapping "Sweet" Spots



Composition Spread Fabrication



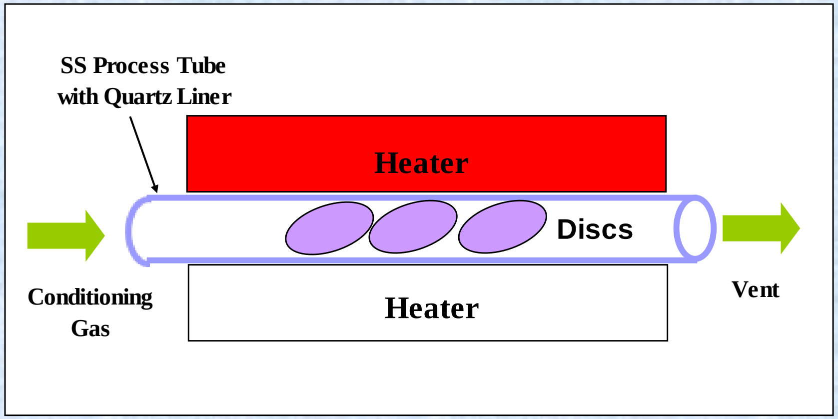




A continuous spread of ternary alloys are synthesized at once into a single thin film

Quick, high throughput

Testing Composition Spreads in Coal Gas



- A setup was built to expose composition spreads to typical coal gas conditions
- H_2 17.6%, CO_2 17.9%, CO 2.6%, H_2O 2.6%, N_2 59.3%, and H_2S 169 ppm
- 350°C for 24 hrs at 1 atm
- Visually examine if any spots across composition spread film still appear metallic and shiny

▪Volume Percent

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Raman Microscopy for High Speed Screening

Equipment

- DXR Confocal Raman Microscope
- Objectives x10, 20, 30, 50, 100

Specifications

- Dispersive Raman microscopy
- Excitation sources 532 or 780 nm
- Scan range 50 - 3400 cm^{-1}
- CCD detector
- Spectral resolution 2.4 - 4.1 cm^{-1}
- Spatial resolution ~1 micron
- Motorized mapping stage

Progress and Status

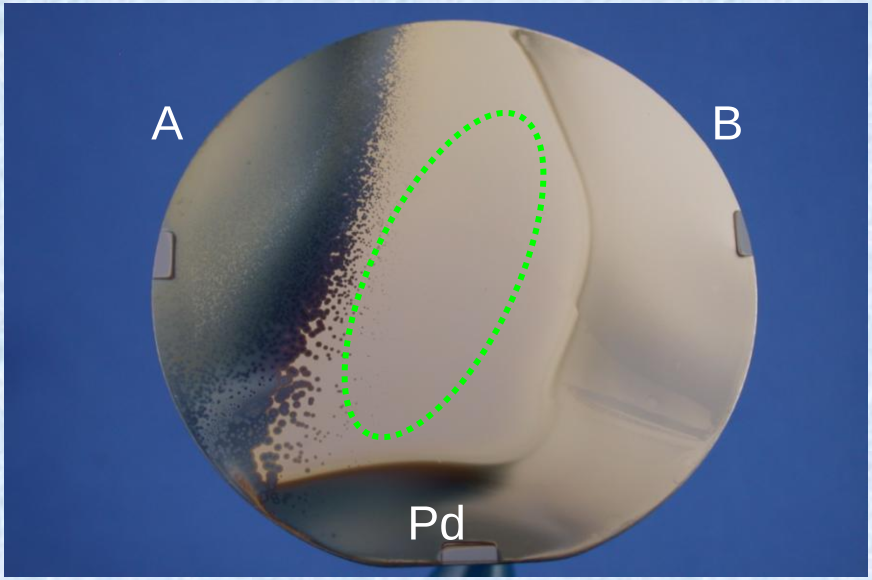
Task 3.0	Design and modeling of binary and ternary palladium alloys for use as high temperature, high pressure gas separation membranes under coal gasifier conditions. ▪ Baseline testing of Pd-Au membranes to determine the effects of coal gas components and impurities; ▪ Advanced palladium alloy development using combinatorial techniques to identify potential Pd alloys resistant to coal gas environment; ▪ Model hydrogen permeation of candidate palladium alloys using DFT theory.	Dec 1, 2009 to Sept 30, 2010	Extended due to contract negotiations

Tested Nine Ternary Composition Spreads

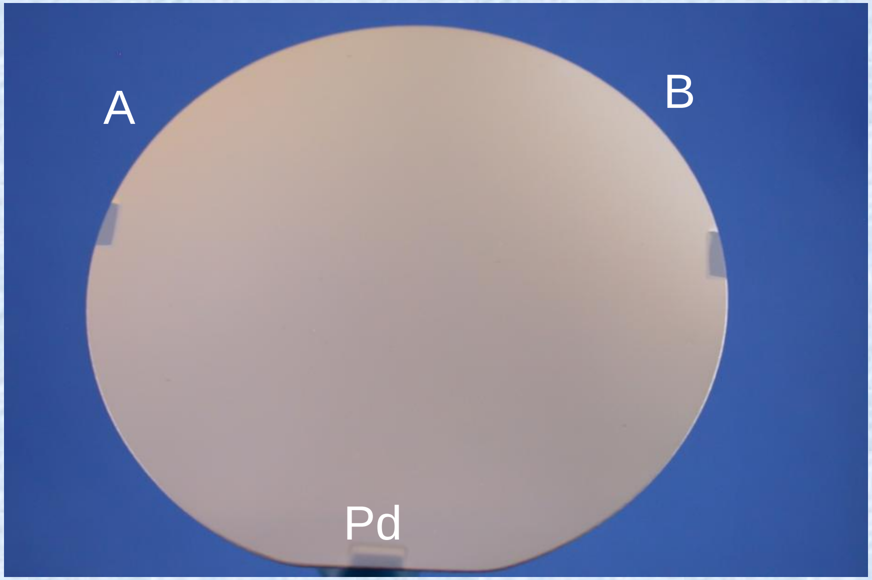
- Five Pd-Au-X composition spreads
- Two Pd-Ag-X composition spreads
- Two Pd-Cu-X composition spreads

Visual Screening Example 1

Spread Pd-A-B: Coal Gas Exposure



Spread Pd-A-B: No Exposure

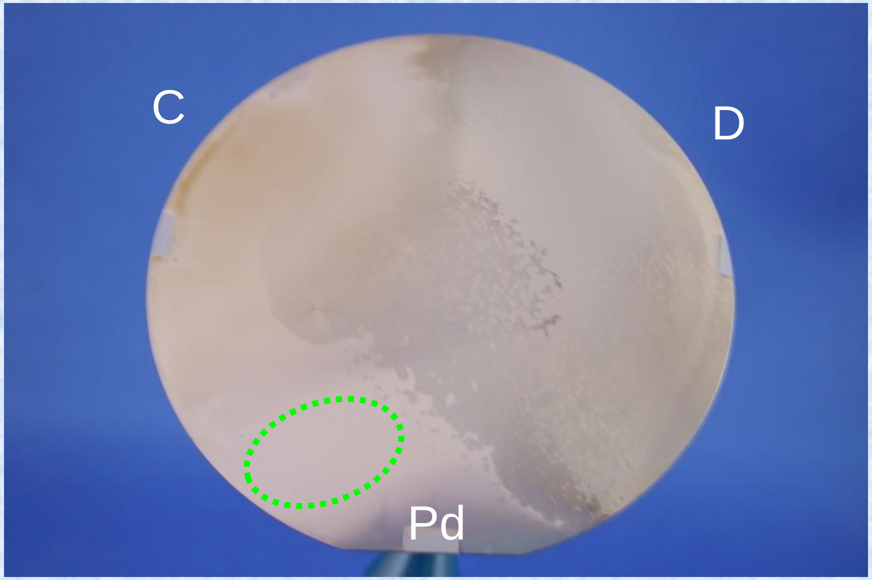


Balanced range A and B

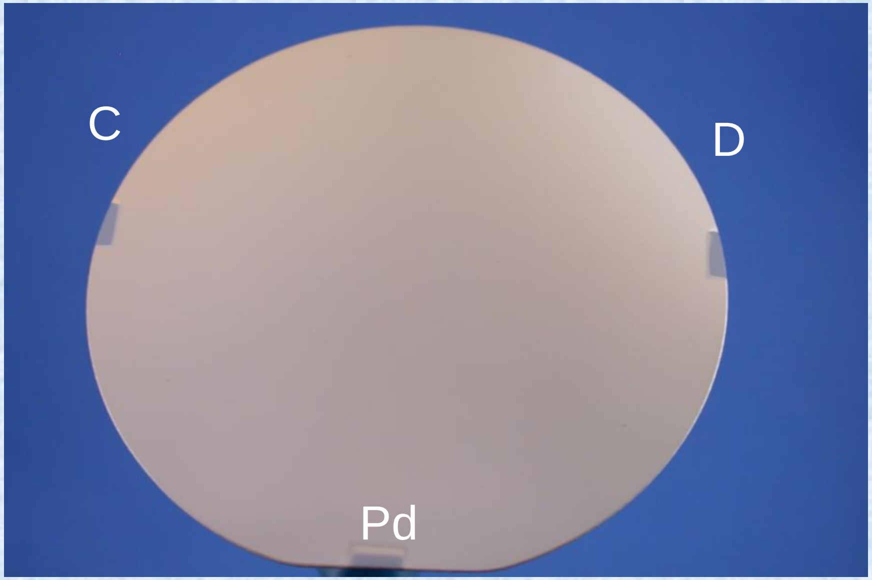
Low to high level of Pd

Visual Screening Example 2

Spread Pd-C-D: Coal Gas Exposure



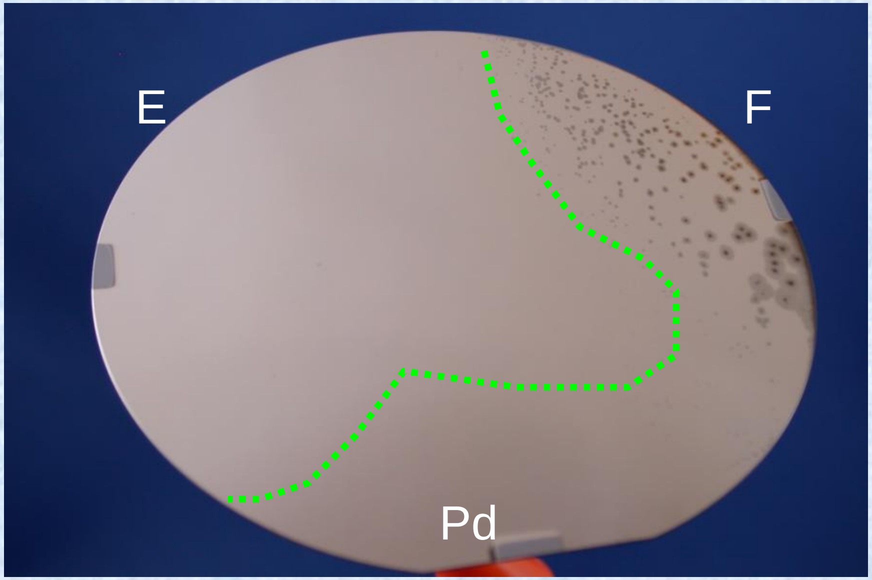
Spread Pd-C-D: No Exposure



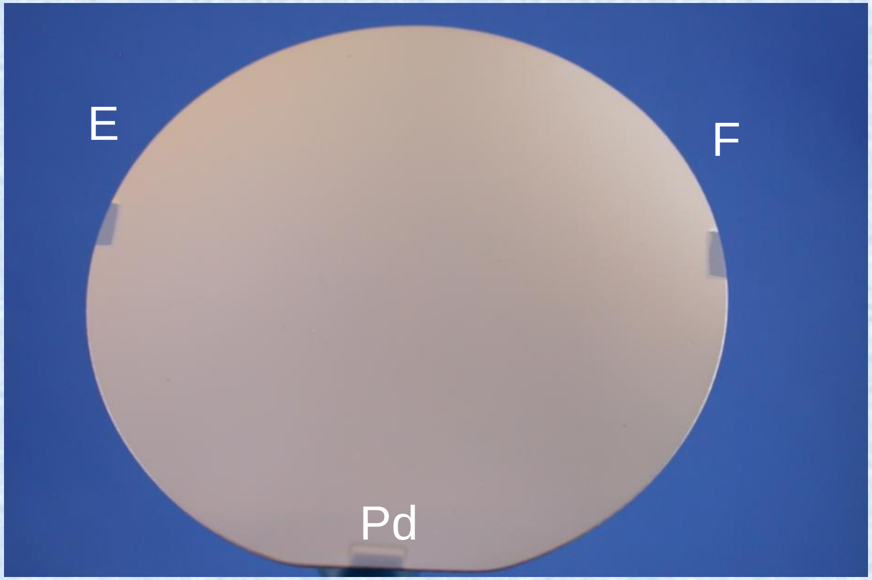
Small range of unaffected surface
Demonstrated hydrogen permeability

Visual Screening Example 3

Spread Pd-E-F: Coal Gas Exposure



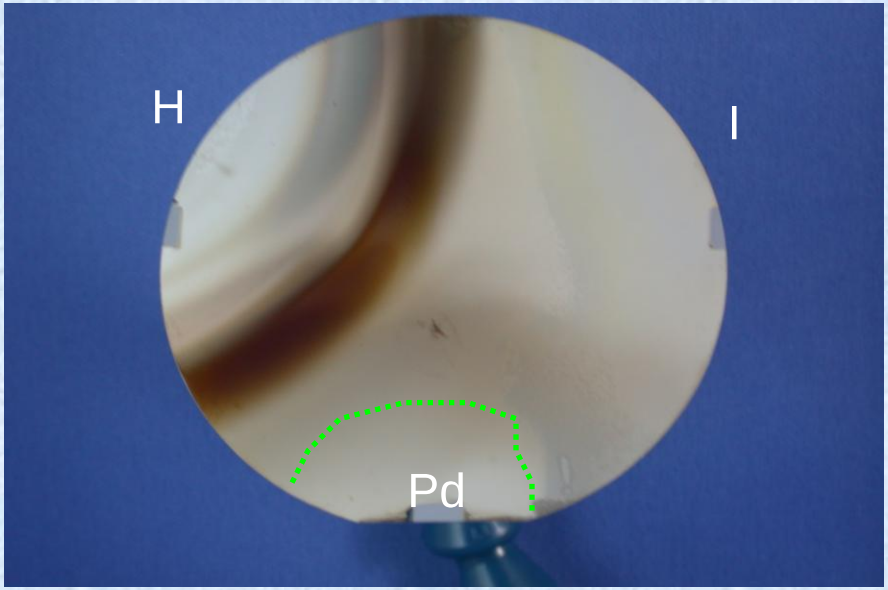
Spread Pd-E-F: No Exposure



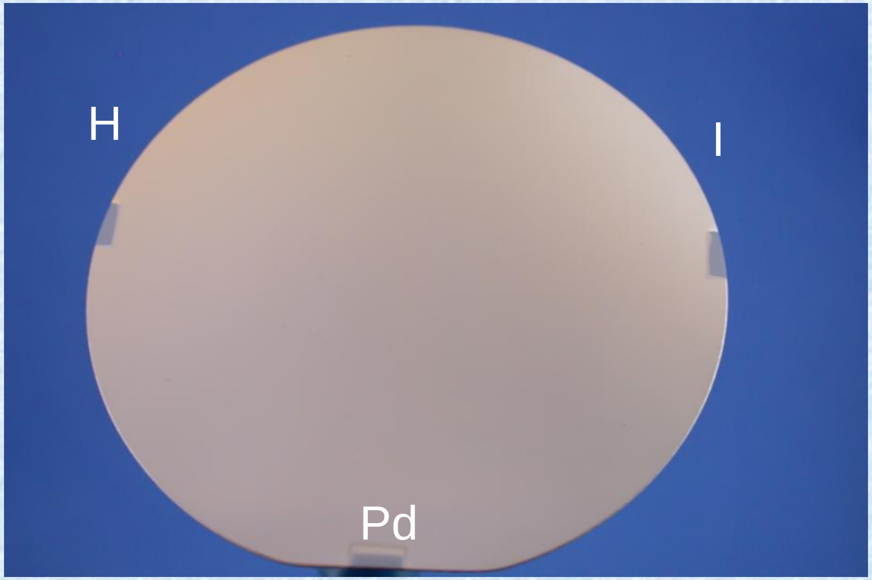
E-rich Pd alloys

Visual Screening Example 4

Spread Pd-H-I: Coal Gas Exposure



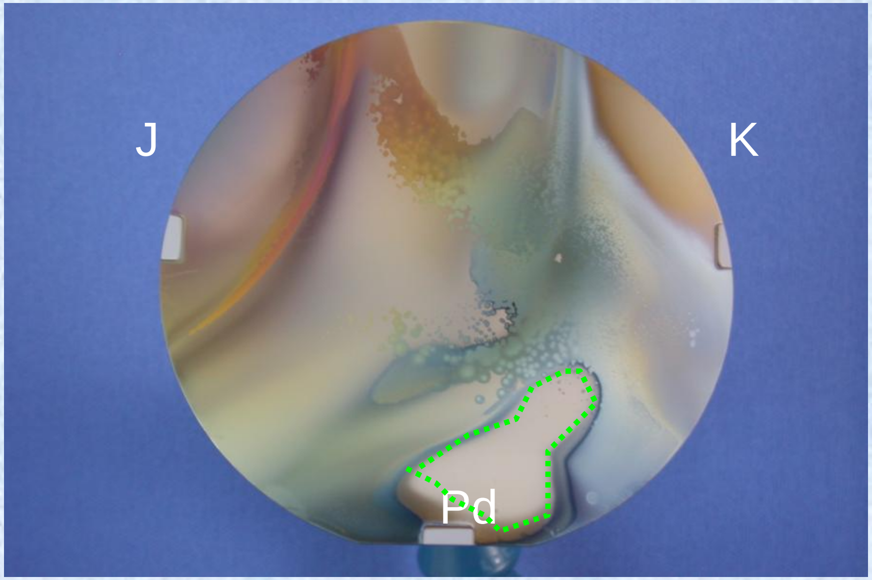
Spread Pd-H-I: No Exposure



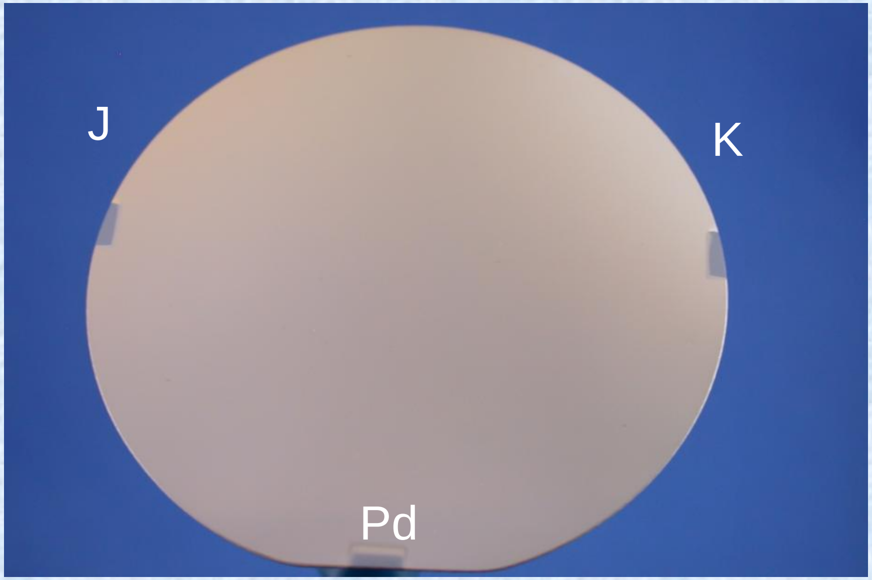
H and I – promoted Pd – rich alloys

Visual Screening Example 5

Spread Pd-J-K: Coal Gas Exposure



Spread Pd-J-K: No Exposure



A small un-affected area of Pd rich alloys

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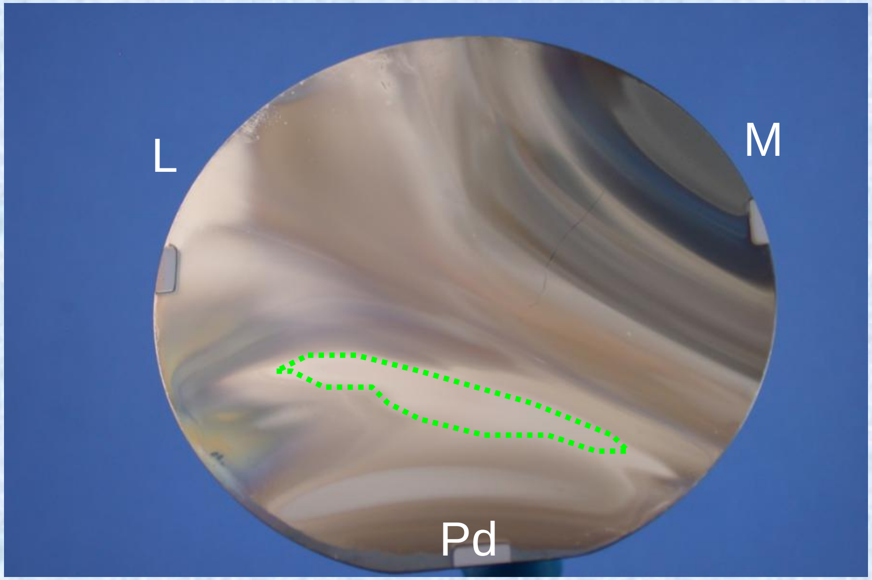
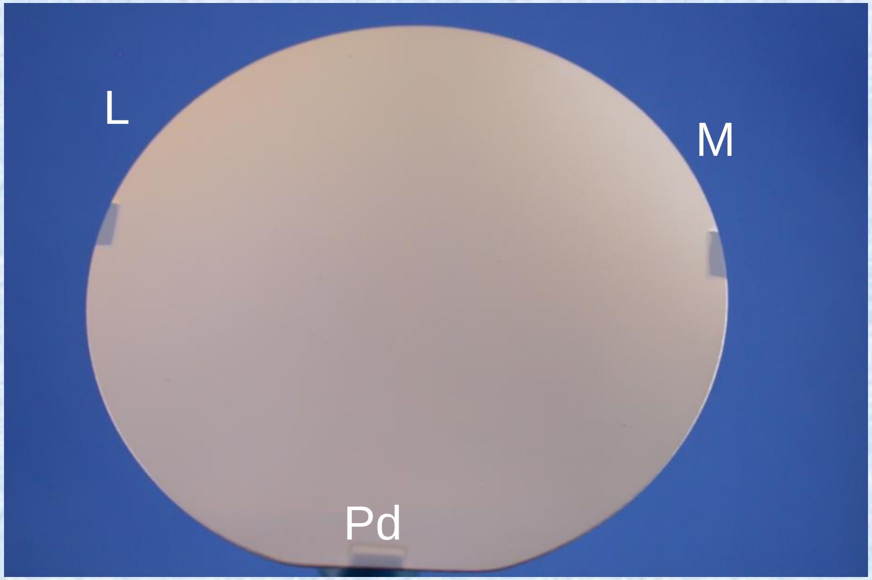
Visual Screening Example 6

Spread Pd-L-M: Coal Gas Exposure



Spread Pd-L-M: No Exposure



Narrow compositional range
Higher Pd level

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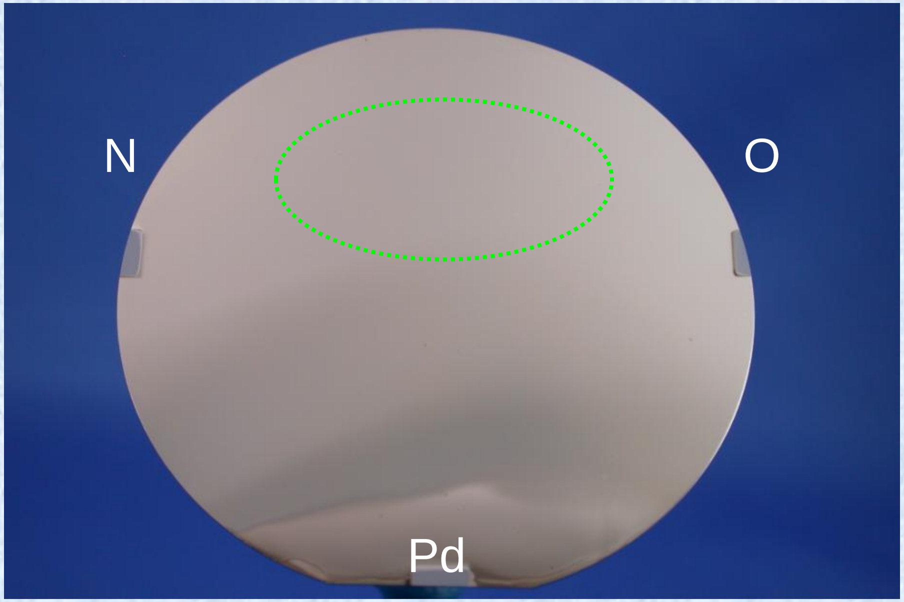
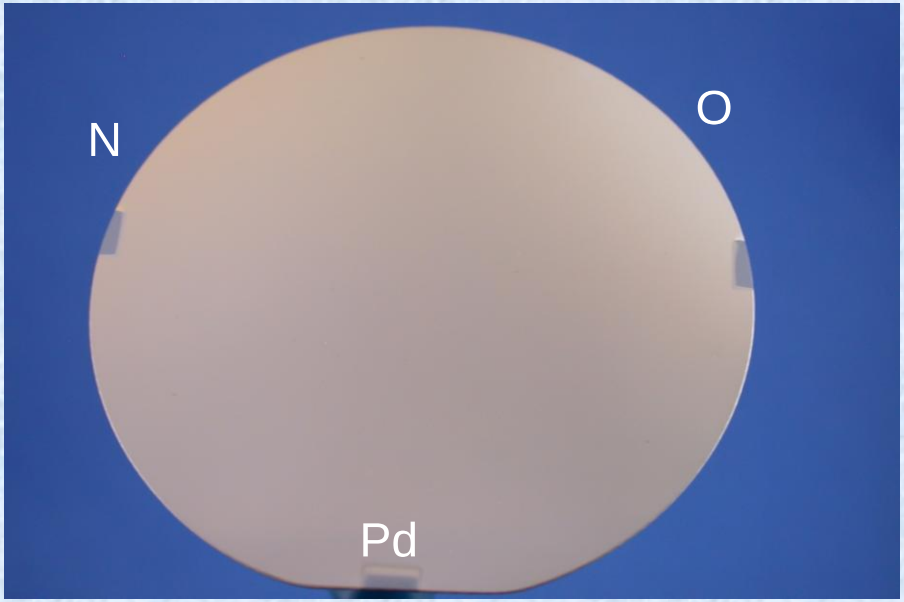
Visual Screening Example 7

Spread Pd-N-O: Coal Gas Exposure



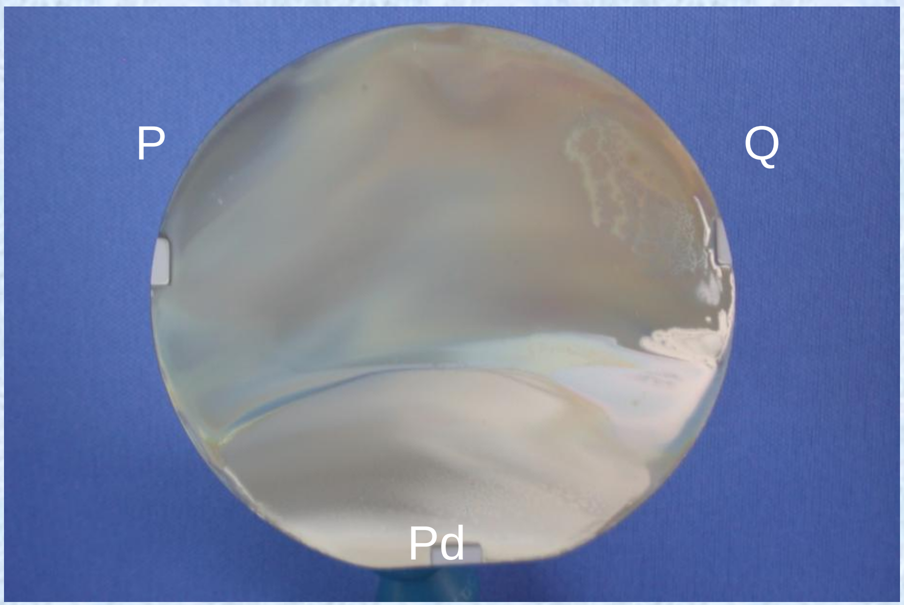
Spread Pd-N-O: No Exposure



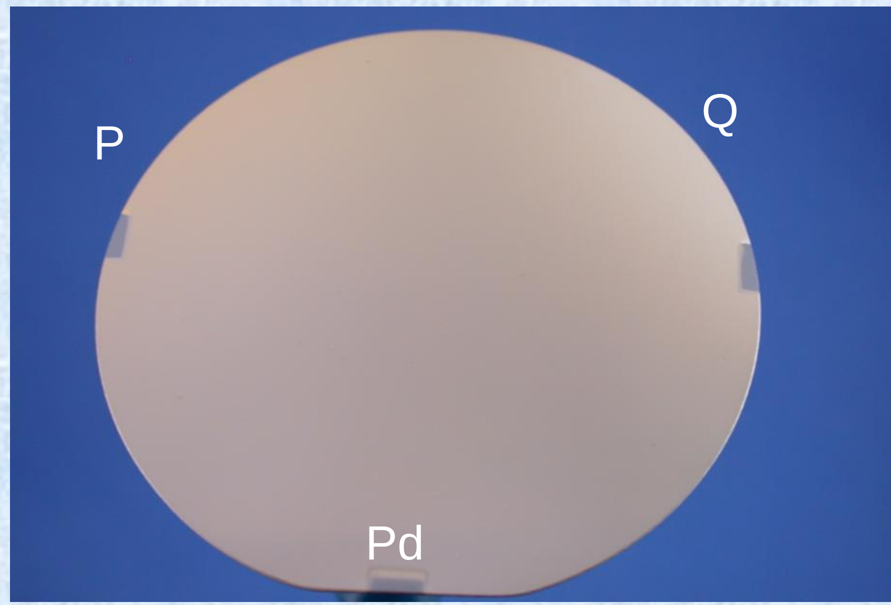
Un-affected low Pd level alloys

Visual Screening Example 8

Spread Pd-P-Q: Coal Gas Exposure



Spread Pd-P-Q: No Exposure

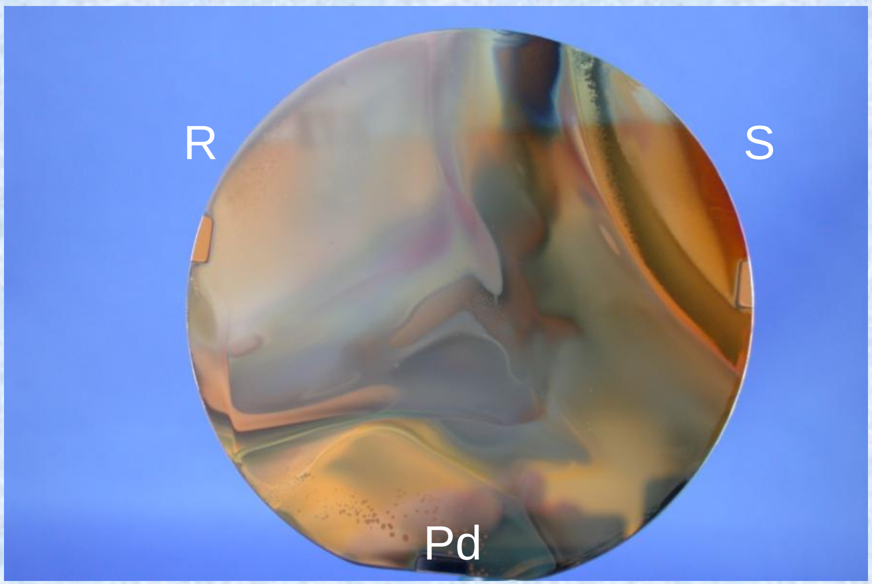


Entire surface affected by coal gas

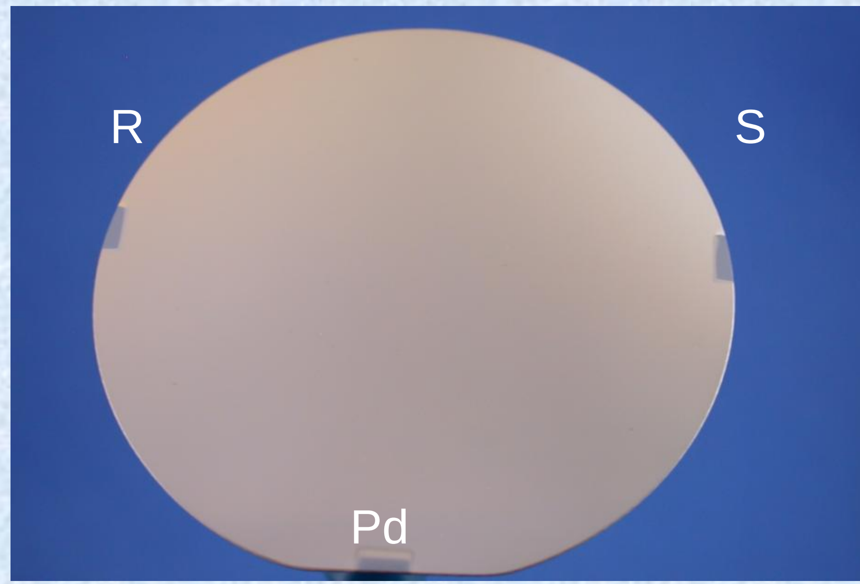
No shiny area visible

Visual Screening Example 9

Spread Pd-R-S: Coal Gas Exposure



Spread Pd-R-S: No Exposure



Entire surface affected by coal gas
No shiny area visible

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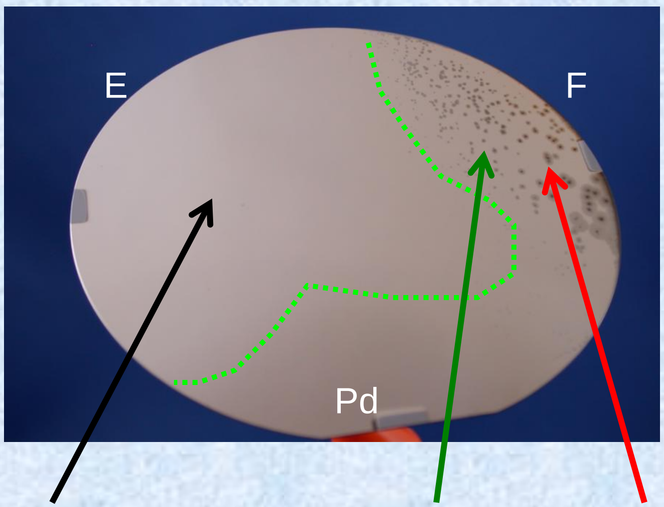
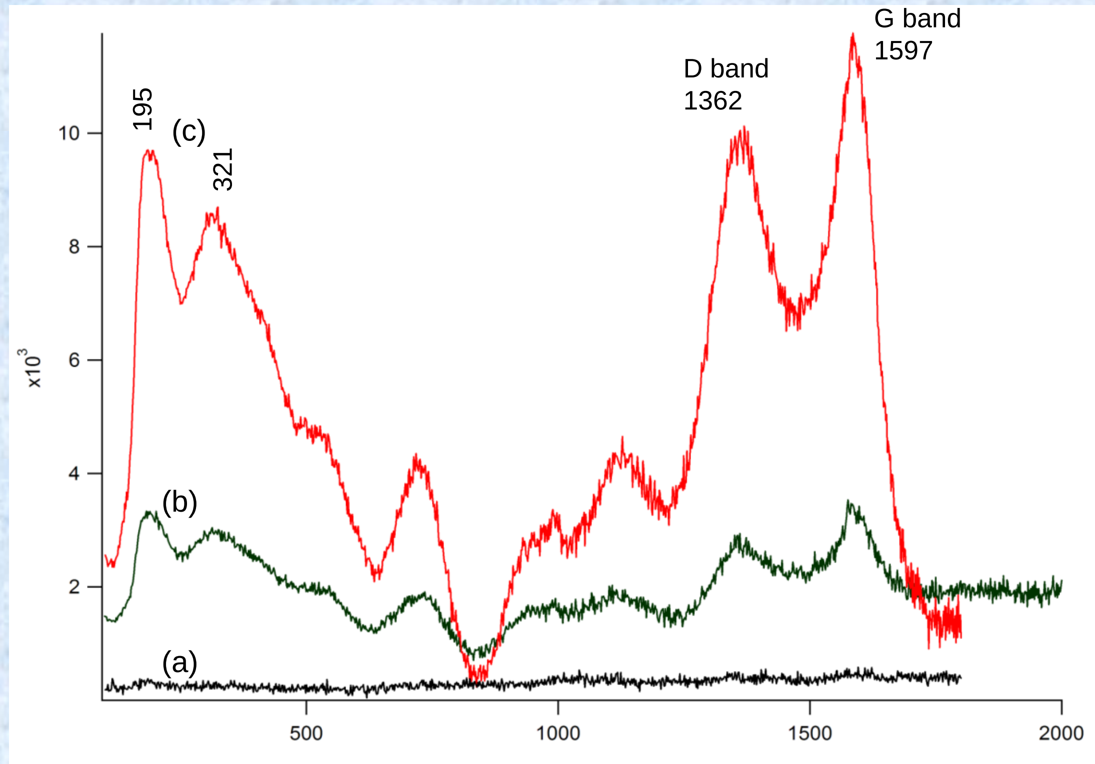
Raman Microscopy as High Throughput Screening Tool: A Example

Spread Pd-E-F: Coal Gas Exposure

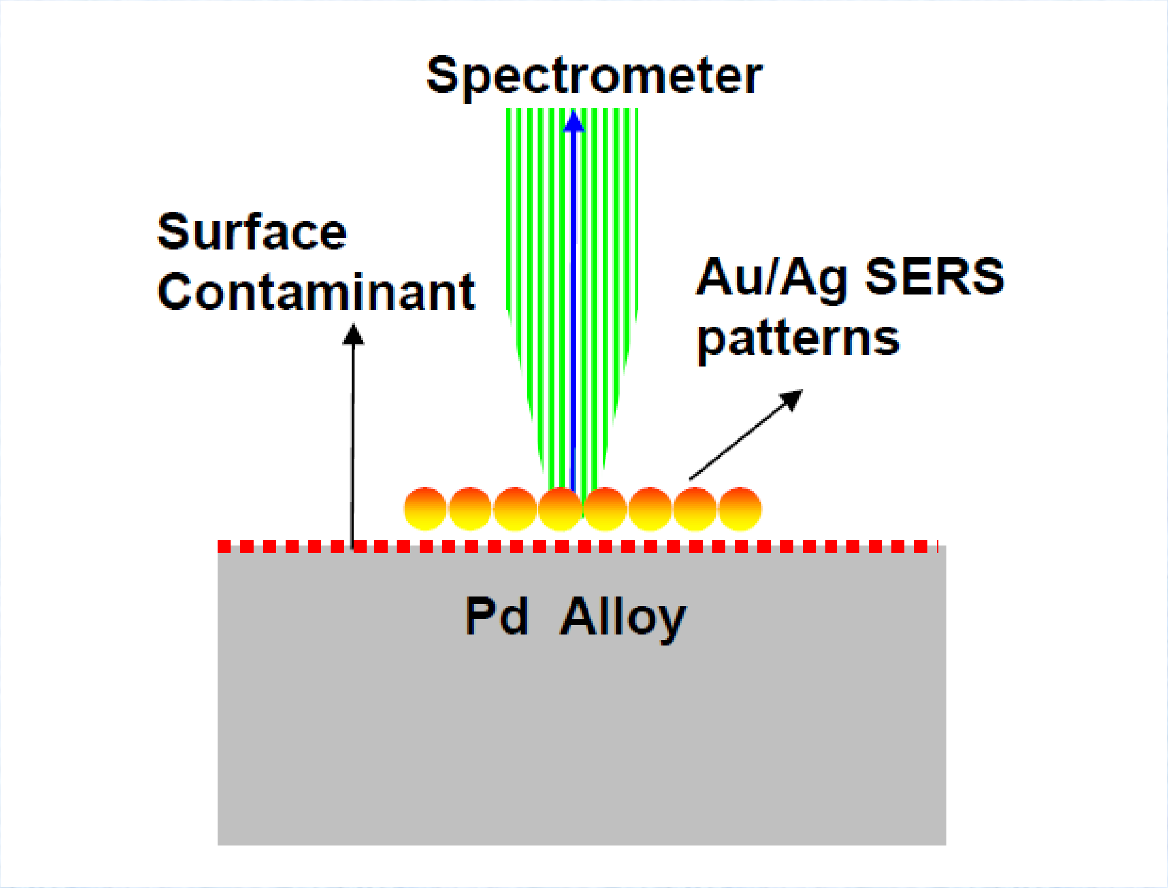


Shiny Spot Between Black Spots Black Spot



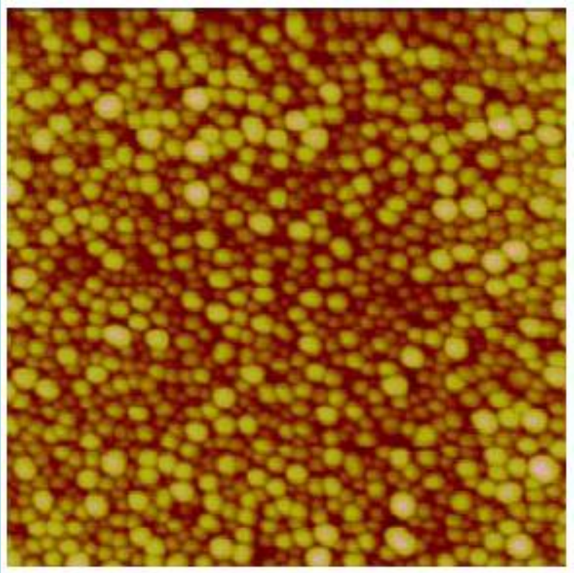
How to Improve Raman Sensitivity

Surface Enhanced Raman Scattering (SERS) By Nano Particles Coating

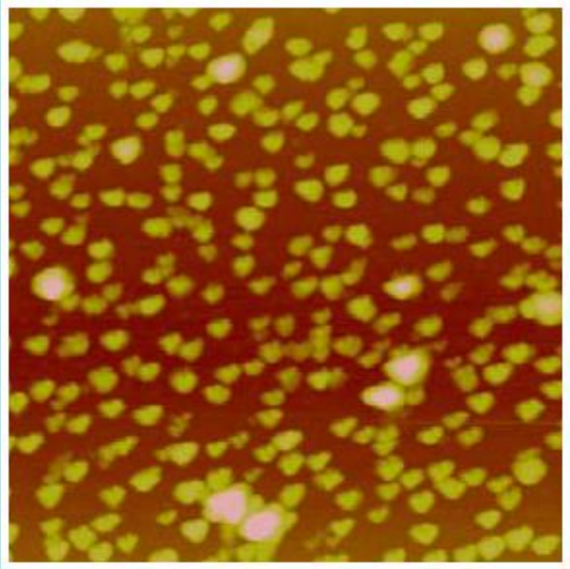


Nano Silver Particles Coating: AFM Images

Coating by Sputtering



Coating by Colloid



- Silver coating by sputtering is quite similar to one by colloid spinning process
- Sputtering deposition is clean process without need to post-coating treatment, which may modify surface of sample

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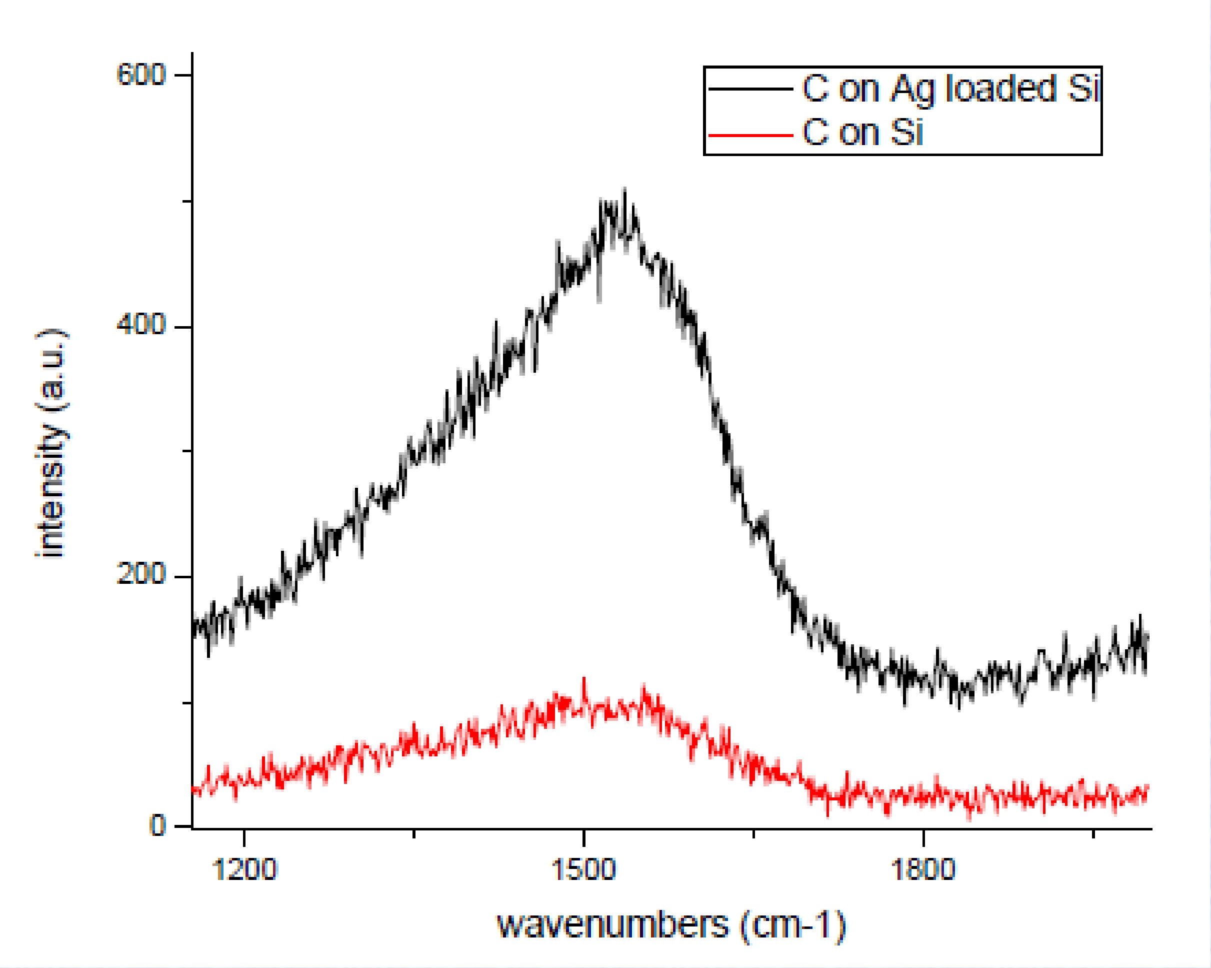
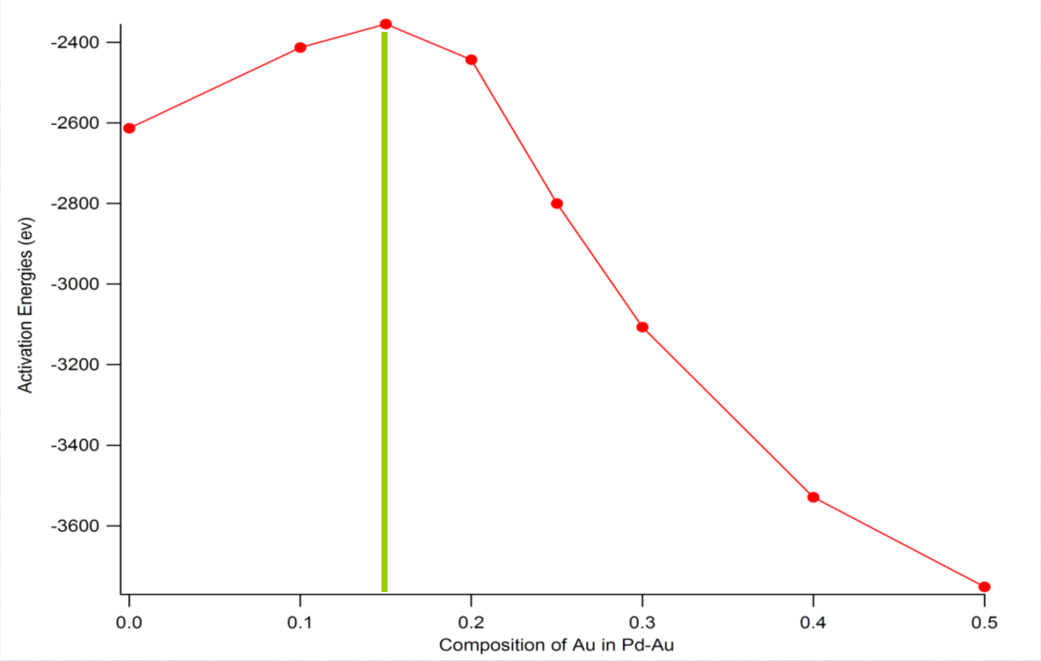
Raman Signal Enhancement by Nano Silver Coating

Carbon as Probe



H_2 Transport Modeling: Pd-Au Alloys

Au 15atm% minimum activation energy for H_2 transport at 293K*



Approach

DFT calculations (VASP code) for predictions of the energies of H inside bulks of pure Pd and Au, and Pd-Au with 75%Pd-25%Au and 50%Pd-50%Au.

Monte Carlo Simulations for predictions of the diffusion rates of H inside bulks of pure Pd and Pd-Au with different composition.

* The calculations are in agreement with experimental results in literature

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Third Year Plans

Task 4.0 Construct and test foils and 15 cm^2 active surface area prototypes of candidate palladium alloys

Task 5.0 Scale up active surface area of membrane from 15 to 75 cm^2

Task 6.0 Construct a working membrane module capable of extended service as a hydrogen separation system under coal gasifier conditions

Task 7.0 Provide complete analysis of relevant data sufficient to permit economic evaluation of the process